Journal of Power Sources 216 (2012) 304–307

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Ac impedance analysis of lithium ion battery under temperature control

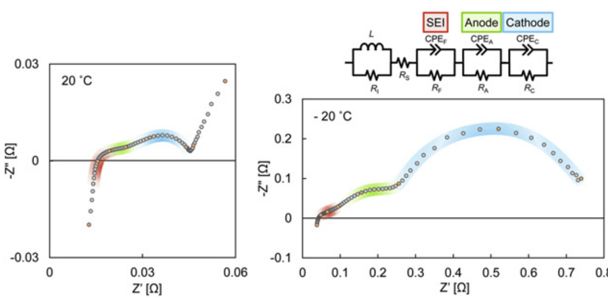
Toshiyuki Momma [a,b], Mariko Matsunaga [b,1], Daikichi Mukoyama [b], Tetsuya Osaka [a,b,*]

[a] Department of Applied Chemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan
[b] Research Institute for Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan

HIGHLIGHTS

► Ac impedance of LIB was measured at low temperature to enlarge the impedance.
► At the temperature below 0 °C another arc of semicircle appeared.
► At 20 °C the hidden arc was found to be small.
► The hidden arc was also overlapping with kinetic impedance and inductive locus.
► The hidden impedance response was attributed to the SEI impedance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 March 2012
Received in revised form
25 May 2012
Accepted 28 May 2012
Available online 5 June 2012

Keywords:
Electrochemical impedance spectroscopy
Lithium ion battery
Low temperature
Enlarged impedance
Time constant
SEI

ABSTRACT

Ac impedance spectra of electrochemical systems are analyzed by considering adequate equivalent circuits, while the differentiation of responses for each elemental step is sometimes difficult. In this study, enlarged impedances were measured by lowering the temperature of a lithium ion battery (LIB) to make the separation of confusing responses easier. The impedance spectra obtained at the temperatures between −20 °C and 20 °C showed drastic change in sizes with shifting of the characteristic frequency. The analysis of impedance spectra using an equivalent circuit revealed changes in resistance of each component and shifting of the time constant for each elemental step. The frequency domain of impedance response of solid electrolyte interphase (SEI) was found to overlap with that of the inductive component of the outer electric lead at 20 °C in our study. The impedance measurement at the low temperatures is considered to be useful for the detection of the SEI and the accurate evaluation of LIB.

1. Introduction

Electrochemical impedance spectroscopy (EIS) has been utilized by many researchers to characterize each factor of batteries because it enables us to analyze the dynamics of each elemental step sensitively and separately without destruction of the cell. In addition, un-destructive EIS is expected to be utilized for premonitory diagnosis of batteries on board in electric vehicles. In our previous study [1,2], the equivalent circuit to express each elemental step in a commercial lithium ion battery (LIB) by EIS was carefully investigated. Also, with the designed equivalent circuit,

* Corresponding author. Department of Applied Chemistry, School of Advanced Science and Engineering, Faculty of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan. Tel.: +81 3 5286 3202; fax: +81 3 3205 2074.
E-mail address: osakatets@waseda.jp (T. Osaka).
[1] Present address: Department of Electrical, Electronic & Communication Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan.

0378-7753/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2012.05.095

impedance responses of LIB during capacity fading by continuous charge–discharge cycling was analyzed, and succeeding rises in impedance of cathode reaction and the solid electrolyte interphase (SEI) were illustrated, while the resistance of SEI in fresh LIB was remarkably smaller than those of the charge transfer reactions at the electrodes/electrolyte interfaces [3].

In actuality, the rapid decrease in the internal resistance of LIB to satisfy the demands for high power and high capacity lead to difficulty in assigning each characteristic in impedance spectroscopy to elementary steps correctly or in precise evaluation of each step having close values in time constants, which sets limits on detail characterization of a battery by impedance spectroscopy.

In order to analyze precisely, enlargement of small impedances and shifting of the overlapping frequency domains are considered to be solutions. The values of resistance and interfacial capacitance are the electrochemical parameters mainly discussed in electrochemical impedance spectroscopy. As the mass transfer of charged carrier has a strong negative correlation with temperature, increases in the resistance of LIB at low temperatures has been reported in the literature [4–6].

In this study, in order to distinguish each response of elemental steps in an LIB reaction, an expansion of impedance of LIB was examined by lowering the temperature. Ac impedance spectra inquired under the temperature range between −20 °C and 20 °C were compared and analyzed.

2. Experimental

A commercially obtained laminated LIB using a carbon anode with a nominal capacity and voltage of 0.8 Ah and 3.8 V, respectively, was examined in this study. The capacity of the LIB was measured and it was found that the voltage of the LIB at the state of charge (SOC) 50% was 3.837 V. The LIB was characterized by EIS at every 5 °C from −20 °C to 0 °C, and at 20 °C. After changing the environmental temperature of LIB, the LIB was kept for 2 h (7200 s) in the incubator before the measurements. The EIS were obtained at the 3.837 V of DC off-set to maintain the SOC value as 50%, with 5 mV of ac signal in the frequency range of 100 kHz–10 mHz. Data fitting was carried out with Microsoft Excel Solver to reach the minimum value of the error by following our previous report [2].

3. Results and discussion

The Nyquist plots obtained from the LIB with SOC value of 50% at various temperatures are shown in Fig. 1. All the impedance loci were revealed to have plots in the fourth quadrant in the high frequency region, which had minus values in $-Z''$, indicating the existence of an inductive component of the outer lead [2], and overlapping semicircles in the lower frequency region. At 20 °C, two semicircles, relatively large and small, were observed at the middle and the higher frequency region, respectively, as in other reports [1–3,7,8]. However, remarkably, another semicircle appeared at the higher frequency region below 0 °C by setting careful eye on the plots, and the size of the new one was observed to increase with the two others by decreasing temperature of the LIB, T. Namely, the semicircle at the higher frequency, which was not detected by the eyes at T of room temperature, is considered to be apparently detectable by setting T as the low temperatures.

In addition, the impedance spectrum at 20 °C remained unchanged when T was returned from −20 °C to 20 °C. Thus, temperature was assessed not to irreversibly change the intrinsic properties which can be observed in the Nyquist plots. According to our previous report [2,3], an equivalent circuit, shown in Fig. 2(a), which had three RC parallel connections of SEI film, anode, and

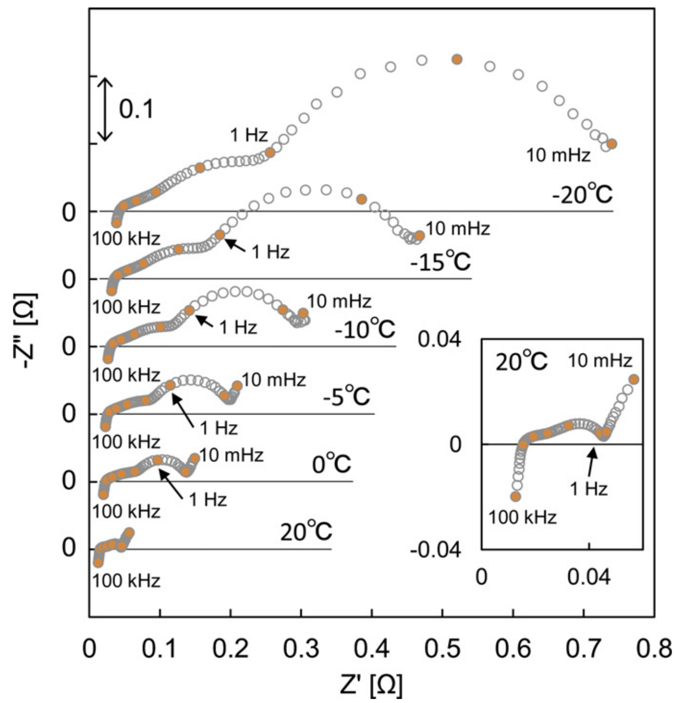


Fig. 1. Nyquist plots obtained by electrochemical ac impedance for a lithium ion battery at 20, 0, −5, −10, −15, −20 °C. Each parallel line shows 0 Ω of Z″ at each temperature. Inset is the magnified Nyquist plots for 20 °C.

cathode, was designed. The overlapping semicircles obtained in the frequency range between 10 kHz and 10 mHz, shown in Fig. 1, were analyzed. In this study, the impedance response corresponding to the diffusion process was ignored due to the limitation of the frequency range. The Nyquist plots were simulated to estimate R and C values of each elemental process at various T using the equivalent circuit, and all the spectra were well fitted.

The equivalent circuit used in this study, three sets of resisters and capacitors connected in parallel were connected, which had three unique time constants. With the parameter fitting using the circuit for the obtained impedance results, three sets of time constants were found to be determined for the results obtained by varying the temperature. According to our previous study, the sets of resisters and capacitors with the values of time constants obtained for the impedance results measured at 20 °C of about 3×10^{-5}, 6×10^{-4}, 3×10^{-2} s were assigned to be the impedance components of the SEI, the anode, and the cathode, respectively, while in our previous work on a different LIB, the values of time constant for SEI, the anode and the cathode were about 4×10^{-5}, 7×10^{-3}, 5×10^{-2} s [2,3].

The values of R and C are shown in Fig. 2 (b) and (c) with a function of T. Each resistance value, R, is demonstrated to increase by decreasing the T. By focusing our attention on the value of R, it should be noted here that the resistance of the SEI, R_F, at 20 °C was obtained as 1.0×10^{-3}, while R_A and R_C were 1.6×10^{-2}, and 1.7×10^{-2} Ω, respectively. From this result, R_F is considered to be too small to be separated from the other larger semicircles for reactions of anode and cathode as well as what is predictable from the appearance of the Nyquist plots. Another point to be noted is that with the extrapolation of the plots of temperature towards room temperature, the R value might be estimated even at a small value. On the other hand, the capacitances, C, did not change much with T, except for the capacitance of the SEI, C_F. The results for anode and cathode suggest that any structural change producing variation of the value of capacitance does not occur by altering T.

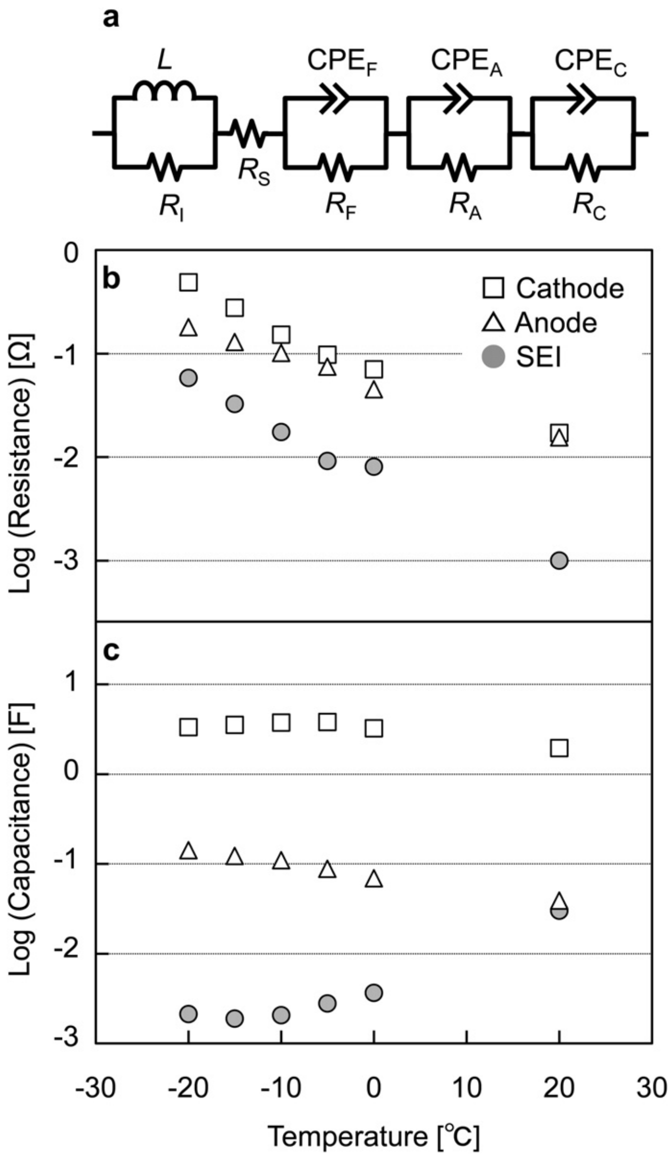


Fig. 2. The equivalent circuit designed to analyze the impedance of LIB (a), and obtained electrochemical parameters of resistance (c) and capacitance (b), by fitting to ac impedance data measured at various temperatures using the equivalent circuit. Symbols are expressed as follows: L, R_I, inductance and resistance of battery lead and connected cable; R_S, R_F, resistance of electrolyte and SEI; CPE_F, constant phase element of SEI; R_A, R_C, charge transfer resistance of anode and cathode; and CPE_A, CPE_C, constant phase element of electrode surface of anode and cathode.

The variation of the time constant is also illustrated in Fig. 3. From the figure, it is clearly indicated that all the time constants are separated at every T. The values of time constant for components of SEI, cathode and anode between −20 and 0 °C are separated more than two orders, which is a sufficient separation in the Nyquist plot, while at 20 °C, individual values for the SEI and anode are relatively close to each other, 3×10^{-5} and 6×10^{-4} s, respectively. In addition, the frequency region corresponding to the time constant of 3×10^{-5} s suggests that the impedance response of the SEI appears in the frequency region of 1 MHz–1 kHz, which is the same as the domain of the impedance with minus values of Z'', i.e., the frequency region where the inductive parameters were dominating. Also, the shifting of the time constants by changing the temperature enables separation of the impedance of SEI from the inductive component.

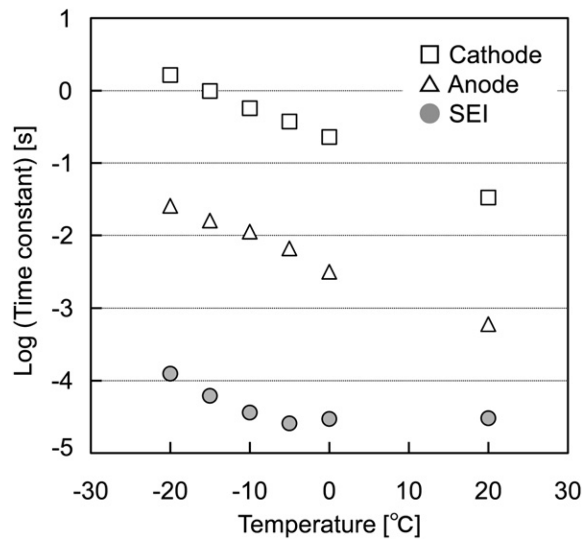


Fig. 3. Variation of time constants of the impedance responses calculated from resistance and capacitance, shown in Fig. 2, for SEI and reactions of anode and cathode.

Considering the change of capacitance values in SEI component and the similar values of three time constants for SEI component in the temperature range above −5 °C, there might exist some experimental errors in parameter fittings for SEI component due to the small R value and overlap of ac response with inductive response in the temperature region.

Here, the reason why a semicircle appeared clearly only at the low T is considered to be as follows: (I) overlap of the frequency range of the impedance for the SEI with that of inductive component, (II) relatively close time constants of each element, or (III) the small value of resistance of the SEI. From these considerations, the EIS measurement at the low temperatures, which is considered not to change the intrinsic properties irreversibly, can be useful for the detection of the SEI and the accurate evaluation of LIB. It is clear that lowering the temperature leads the shifts of time constants and the enlargement of resistance in electrochemistry of LIB.

4. Conclusion

Commercially available LIB was investigated with EIS under various temperatures between −20 °C and 20 °C. Using an equivalent circuit, which was composed of components for cathode, anode, SEI and inductive lead, the impedance responses were analyzed. The SEI element was remarkably detected as a semicircle at the lower T below 0 °C. At 20 °C, the frequency domain, where the SEI impedance would appear, was found to overlap with that of the inductive component and close to that of the cathode reaction. Also the value of the resistance of SEI at 20 °C was found to be small. Temperature control, which leads to a shift of time constants and enlargements of impedances, would be a powerful tool in impedance analysis of LIB.

Acknowledgments

This work was supported by “Research & Development Initiative for Scientific Innovation of New Generation Batteries (RISING)” from New Energy and Industrial Technology Development Organization (NEDO) of Japan and a Grant-in-Aid for Specially Promoted Research “Establishment of Electrochemical Device Engineering” from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).

References

[1] T. Osaka, S. Nakade, M. Rajamaki, T. Momma, Journal of Power Sources 119 (2003) 929–933.
[2] T. Osaka, T. Momma, D. Mukoyama, H. Nara, Journal of Power Sources 205 (2012) 483–486.
[3] D. Mukoyama, T. Momma, H. Nara, T. Osaka, Chemistry Letters 41 (2012) 444–446.
[4] H.-M. Cho, W.-S. Choi, J.-Y. Go, S.-E. Bae, H.-C. Shin, Journal of Power Sources 198 (2012) 273–280.
[5] S.S. Zhang, K. Xu, T.R. Jow, Electrochimica Acta 49 (2004) 1057–1061.
[6] Y. Mita, Y. Kobayashi, S. Seki, Y. Ohno, H. Miyashiro, CRIEPI Report (2008) Q07023 (in Japanese).
[7] G. Nagasubramanian, Journal of Power Sources 87 (2000) 226–229.
[8] D. Zhang, B.S. Haran, A. Durairajan, R.E. White, Y. Podrazhansky, B.N. Popov, Journal of Power Sources 174 (2007) 1001–1006.